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CONTRACT REPORT

Identification and Characterization of Manganese in Canada

FINAL REPORT

Department of Energy, Mines and Resources
CANMET
Mineral Sciences Laboratories

ONTARIO RESEARCH FOUNDATION

REQ.NO.1-9066

CONTRACT REPORT NO. OSQ81-00150

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DSS File No. 26 SQ 23440-1-9066
ORF Contract No. 77001

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May 14, 1982

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PREFACE

At present, Canada is completely dependent on imports of manganese ore supplies from off-shore countries to produce a variety of manganese products including ferroalloys, oxide and chemicals.

This report is aimed at determining potential supply problems, delineating substitute materials and suggesting research efforts to extract manganese values from domestic low-grade ores and waste slags on a profitable basis.

1. PRINCIPAL MANGANESE PRODUCTS AND PROCESSES

1.1 Ferroalloys and Metallic Manganese

The most important and least expensive (25¢/lb Mn) addition agent to steel and iron is high-carbon or standard ferromanganese containing typically 78-80% Mn, 12-14% Fe and 6-7% C. This alloy is saturated with respect to carbon, with manganese and iron values both present as metallic carbides. The level of residual elements amounts to Si up to 2%, P up to 0.35%, S up to 0.05% and As up to 0.30%. Impurity levels are controlled by choice of ores and operating practice.

Since 1978 the widely used blast furnace method has been discontinued in the U.S., Japan and is rapidly declining in Europe. The primary reason is excessive energy consumption when compared with submerged-arc smelting as shown in Table I.

TABLE I

COMPARISON OF ENERGY CONSUMPTION FOR MAKING H. C. FERROMANGANESE. BLAST FURNACE VERSUS SUBMERGED-ARC SMELTING

	kWh/ton Product	Kg Coke/ton Product	
Blast furnace Manganese W. German Practice 1968	nil	1323	(1)
Blast furnace Manganese U. S. Average 1967	nil	1451	(2)
Blast furnace Pig Iron U. S. Average 1967	nil	576	(2)
Submerged-Arc Smelting-Manganese	2200	417	(3)

Based on current prices for electricity (3¢/kWh) and coke ($140/ton) there is a real advantage in favour of the electric furnace method.

A submerged-arc smelting furnace is continuously fed with an ore blend, coke as reducing agent and lime/dolomite flux. Metal and slag are intermittently tapped. An increase in power to the furnace will increase the throughput of materials. The temperature of the smelting operation is controlled by the slag composition. The electrode tip-to-hearth distance is most critical for effective furnace operation and is controlled by the resistivity of the furnace feed and current draw at a given power input. Typical ferroalloy and metal compositions containing manganese are shown in Table II.[1,3]

The slags derived from this operation run as high as 45% MnO. This yields smooth furnace operation, low power consumption at low operating temperatures (at 1400°C) and the Mn recovery into the metal is approximately 80% with low levels of Mn - losses in the gas phase. Typical operating data[3] are shown in Table III. The resulting high MnO slags are low in phosphorus and are processed primarily for making silicomanganese (65 to 70% Mn, 14 to 20% Si and 1.5 to 2.5% C). The resulting discard slag contains 7 to 17% MnO.

The production of a discard slag directly from the standard ferromanganese operation is difficult and requires much higher temperatures, thus higher power consumptions, and greater Mn losses in the gas phase. However, Mn recovery into the metal can be increased and the MnO level in the slag decreased to 20 to 25% MnO.

In making silicomanganese and ferromanganese silicon, there is an inverse relationship between silicon and carbon levels in the metal. At 16% to 18% silicon the corresponding carbon level is approximately 2%, whereas at 30% to 32% Si the carbon level drops to less than 0.1%.

TABLE II

TYPICAL METAL AND FERROALLOY COMPOSITIONS CONTAINING MANGANESE

	Mn	C	Si_{max}	P_{max}	S_{max}	As_{max}	Melting Range (^{o}C)
H.C. Ferromanganese	75-82	6-8	1.2-1.5	.35	.03-.05	.30	1070-1260
M.C. Ferromanganese	80-85	.5-1.5	1.5	.30	.02-.03	.15	1250-1260
L.C. Ferromanganese	85-90	.07-.5	1.0-2.0	.2-.3	.02	.10	1250-1260
Silicomanganese	65-68	2	16-18.5	.2	.04	.10	1075-1320
Ferromanganese-Silicon	63-66	.08	28-32	.2	.04	.15	
Electrolytic Manganese	90.9	<.01	<.01	.01	.04	-	
Aluminothermic Mn-Metal	95-98	<.03	<.05	.05	.008	-	1200-1240
Massive Manganese	93-98	.12-.14	.06-.15	.01-.16	.02	-	

TABLE III

TYPICAL OPERATING DATA
H.C. FeMn FURNACE, 3-1.9m ELECTRODES[a]

	Value
Operating Load, MW	30-35
Apparent Power, MVA	58.9-61.6
Power Factor	0.51-0.57
Electrode Current kA	130
Single-Phase Resistance, mΩ	0.592-0.690
Secondary Voltage, V	262-274
Corrective Capacitors for 0.95 power factor, MVAr	32.3
High Mn Slag Practice	
usage per ton alloy	
Mn ore, t dry	1.969
Coke, t dry	0.417
Electrode paste, kg	8.0
Power, kW·h	2200
ratio, slag to alloy	0.45
slag composition %	
MnO	38.7
SiO_2	24.7
Al_2O_3	14.4
CaO	13.0
MgO	2.7
alloy composition %	
Mn	79.0
Fe	13.0
Si	0.3
C	6.7
Mn recovery	
alloy	83.2
slag	13.8
fume, etc.	3.0

[a] Assuming single-phase reactance = 1.0 mΩ.

Ferromanganese (low silicon level) of low and intermediate carbon levels is generally produced by reacting molten silicomanganese with an ore-lime melt. Silicon in the metal reacts with MnO in the melt producing low-carbon manganese. This reaction can be carried out in the furnace crucible or in the ladle. One of the more common process techniques is shown in Figure 1 [3].

Electrolytic manganese is being produced from ores or slags employing H_2SO_4 leaching [3,4]. The pregnant solution (pH 3) is neutralized to pH 6 to 7 to remove the bulk of iron and aluminium. Trace elements such as As, Cu, Zn, Pb, Co and Mo are removed as sulphides. The purified aqueous solution is electrolyzed in a diaphragm cell at power consumptions of 8 to 9 kWh/kg metal. Typical process parameters and metal compositions are shown in Tables IV and V.

Fused salt electrolysis was practiced in the U.S. to produce Massive Manganese containing 93% Mn, 6% Fe and 0.14% C.[5].

Metallothermic reduction of high grade manganese ores employing aluminum yields 95 to 98% Mn containing 1.5% Al.

1.2 Manganese Dioxide

Electrolytic manganese dioxide (EMD) is produced from aqueous sulphate solutions according to the overall reaction $Mn^{2+} + 2H_2O \rightarrow MnO_2 + 2H^+ + H_2$. The EMD type product functions well as a solid-state oxygen electrode in dry-cell batteries. The current efficiency in the electrolysis step is 90-95% and 0.45 kWh/kg EMD are required. A typical flow sheet[6] is shown in Figure 2.

FIGURE 1

Flowsheet for Making
Medium Carbon Ferromanganese

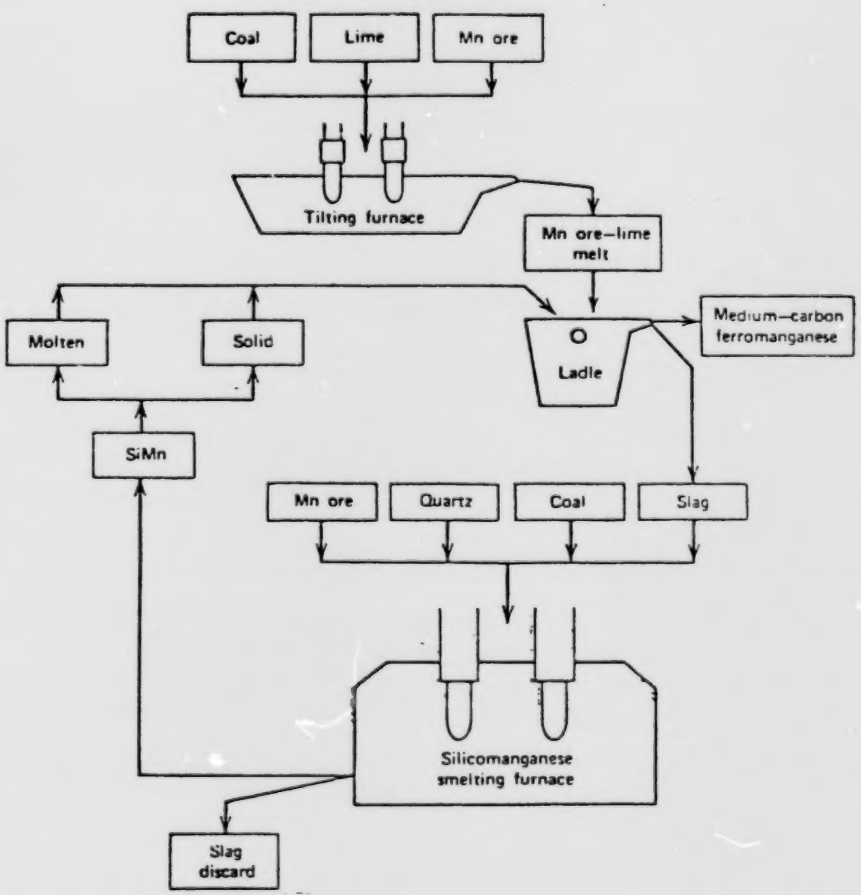


TABLE IV

ELECTROLYSIS OF MANGANESE ORE - PROCESS CONDITION

Condition	Value
Purified Feed Solution, Catholyte	
Mn as $MnSO_4$, g/L	30-40
$(NH_4)_2SO_4$, g/L	125-150
SO_2, g/L	0.30-0.50
Anolyte	
Mn as $MnSO_4$, g/L	10-20
H_2SO_4, g/L	25-40
$(NH_4)_2SO_4$, g/L	125-150
Current Density, mA/cm^2	43-65
Catholyte pH	6-7.2
Anode Composition	Pb +1% Ag
Cathode Composition	Hastelloy, Type 316 Stainless Steel, or Ti
Cell Voltage, V	5.1
Diaphragm	Acrylic[a]
Current Efficiency, %	60-70

[a] Usually specified as to porosity

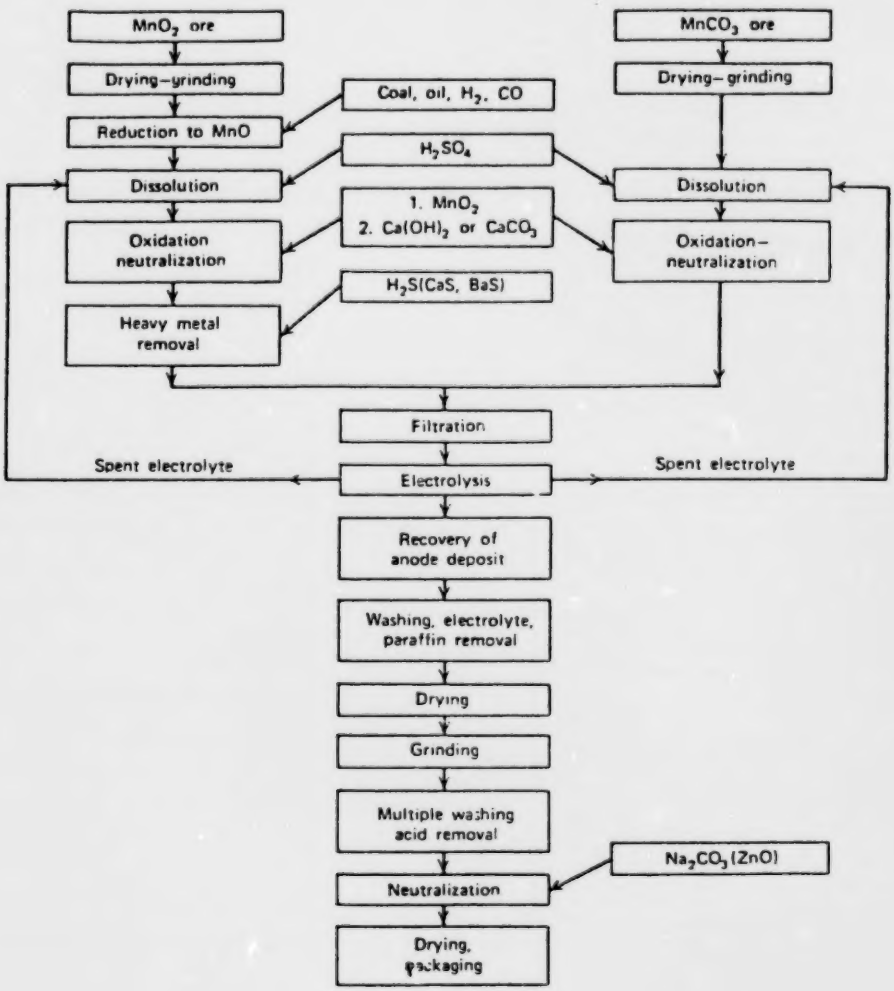
TABLE V

IMPURITIES IN ELECTROLYTIC MANGANESE METAL

Element	Percent
Fe	0.0015
Cu	0.0010
As	0.0005
Co	0.0025
Ni	0.0025
Pb	0.0025
Mo	0.0010
Sulfide S	0.0170
Sulfate S	0.0140
C	0.0020
H_2	0.0150

FIGURE 2

Electrolytic Manganese Dioxide from Manganese Ores



Chemical manganese dioxide (CMD) is produced:

- by thermal decomposition of manganese nitrate
- by roasting of manganese carbonate in air
- as a by-product of reactions involving permanganate as an oxidant
- by activating native ore with sulphuric acid

1.3 Potassium Permanganate

A two-step process (Carus Chemical Co.)[7] employs MnO_2 which is oxidized in the liquid phase with KOH, air and water. The resulting manganate (K_2MnO_4) is oxidized electrolytically to produce the permanganate product ($K\ MnO_4$).

A three-step procedure [6] converts MnO_2 to K_3MnO_4 at 400°C in the presence of KOH and air employing a rotary kiln. A secondary roast (200°C) produces manganate which is electrolyzed to permanganate.

1.4 Other Manganese Chemicals

Manganese carbonate is prepared from purified sulphate solutions and precipitated with alkali carbonate. Manganese chloride is made by reacting metal oxide or carbonate with hydrochloric acid. Also direct chlorination of Mn metal.

Manganese nitrate is prepared from MnO or $MnCO_3$ with dilute HNO_3 or from MnO_2 employing nitrous (HNO_2) and nitric acids (HNO_3).

Manganese oxide (MnO) is produced by controlled reduction of MnO_2 with CH_4 at 760 - 1040°C.

Manganese sulphate is produced by dissolving MnO or natural carbonate ore in sulphuric acid. At pH 6.5, ferric iron is precipitated together with other impurities. Traces of Zn, Ni, Co, are eliminated with $(NH_4)_2S$ in neutral solutions. Mn SO_4 is recovered as a monohydrate precipitate at 160°C in aqueous solution.

1.5 Summary

There are three main groups of manganese sub-products: Ferromanganese and manganese metal, manganese dioxide and manganese chemicals. These are itemized and a broad outline of the more important of the manufacturing processes are given.

2. CONSUMPTION OF MANGANESE PRODUCTS - APPLICATION AND USE

The consumption of manganese products in Canada and the United States are dependent on imported ores from off-shore countries.

Canadian Consumption [8] of manganese ore in 1978/1979 amounted to:

Application	1978	1979	
Metallurgical Grade	198,560	58,587	tonnes
Battery and Chemical	2,760	3,056	tonnes
TOTAL	201,320	61,643	tonnes

It can be noted that almost all the imported ores are used in the metallurgical industry. (Table XI). Page 21.

Consumption of manganese ore in the United States [3,9] shows a downward trend:

	1972	1975	1977
	In Thousand Tonnes		
Ferromanganese alloys and Metal	1,747	1,307	841
Pig iron and steel	192	160	182
Chemicals, dry cells, Misc.	177	184	210
TOTAL	2,116	1,651	1,233

World consumption of manganese ore in 1977 was 9 million tonnes contained Mn. It is estimated that this will increase at a rate of 2.9%/year to 21 million tonnes contained Manganese by the year 2000. Mn ore prices have increased from U.S. $49/tonne contained Manganese in 1969 to U.S. $138/tonne contained Manganese in 1980.

Breakdown of 1976 world consumption for non-metallurgical uses:

	10^3 tonnes
Dry cell	500
Ceramics	200
Chemical	450
Metal treatment/ welding	200
	1,350

In steel, manganese serves as a desulphurizer to control hot shortness for improving machinability. Secondly it is a good deoxidizer and, most importantly, is a low cost alloying agent to improve strength, toughness, hardenability and abrasion resistance.

On average 5.8 kg of manganese are required to produce a tonne of raw steel. Typical manganese additions to various types of steel are shown in Table VI.

In cast irons manganese desulphurizes and adds strength.

In aluminum alloys manganese imparts strength, hardness and stiffness. For these applications electrolytic manganese is used as well as briquets and master alloys comprising manganese metal and aluminum.

Metallic manganese is also used in low-carbon specialty alloys including pipeline steels and most nickel and cobalt based alloys as well as aluminum and copper bearing materials.

The non-metallic uses of manganese oxides and chemicals are summarized in reference [6] which is mainly based on detailed information published by S. A. Weiss[7] and shown in Tables VII, VIII and IX.

TABLE VI

TYPICAL MANGANESE CONTENT OF RAW STEEL
(KG/t RAW STEEL)

Manganese	Type				
	Carbon	Low Alloy	Full Alloy	Si Sheet	Stainless
Standard Ferromanganese	4.45	7.0	7.05		1.7
Silicomanganese	0.75	0.25	0.05		
Refined Manganese(a)	0.80	1.75		0.60	7.5
Other (b)				0.80	3.5
TOTAL	6.00	9.00	7.10	1.40	12.7

(a) Includes medium carbon and low carbon ferromanganese, electrolytic manganese metal, and various grades of nitrided manganese alloys.

(b) Generally ferromanganese silicon.

TABLE VII

MAIN NONMETALLURGICAL USES OF MANGANESE OXIDES

Compound	Applications	Consumption, 10^3 t World	Consumption, 10^3 t U.S.
Manganese (II) Oxide	Fertilizer	45	18
technical	Feed Additive	27	9
	Intermediate in the Manufacture of electrolytic Mn metal, Mn(II) salts, EMD		
high purity	High Quality Ferrities; ceramics intermediate for higher purity Mn(II) salts such as $Mn(H_2PO_4)_2$ Mn acetate		
Dimanganese Trioxide Trimanganese Tetroxide	High Purity Grades used in production of ferrites, thermistors, and in other electronic applications		
Manganese Dioxides	Colorant in brick and tile manufacturing	136-145	23-27
Native Ores	Colorant in glass making	5	0.5
	Frits		5
	Raw Materials for Most Other Mn Chemicals		
	Hydrometallurgy of Uranium		
	Hydrometallurgy of Zinc	39	
	Welding Rods and Fluxes		21
	Dry-Cell Batteries	185	36
	Oxidant in Chemical Processes		
	Absorbent for H_2S and SO_2		
	Ferrites (lower grade)		4
Activated	Dry-Cell Batteries (Philodyne, Ergogene)	4	
CMD	Dry-Cell Batteries (Type M Permanox, Manganit), oxidant in organic synthesis, high purity MnO_2 for ferrites and thermistors, curing agent for polysulfide rubbers, constituent in oxidation catalysts	18	0.5
EMD	Dry-Cell Batteries, ferrites	100	16

TABLE VIII

USES OF MANGANESE COMPOUNDS

Compound	Applications
Salts of Inorganic Acids	
Carbonate	Intermediate in the synthesis of other Mn salts, such as phosphate, gluconate, acetate, nitrate; for manufacturing of ferrites, welding rods, also as hydrogenation catalyst.
Chloride	Magnesium metallurgy; synthesis of MMT, as brick colorant; textile dyeing, dry cell batteries, chlorination catalyst.
Trifluoride	Fluorination agent.
Hypophosphite	Manufacture of delustered polycondensate fibers, i.e. nylon.
Nitrate	Intermediate in manufacturing of high purity Mn oxides; in production of tantalum capacitors.
Phosphate (monobasic)	Rust-proofing; wear-reduction in moving metal parts (bearings, etc.).
Pyrophosphate	Textile dyeing
Sulfate	Intermediate in manufacture of many Mn products i.e. electrolytic Mn metal, EMD, Maneb, Mn soaps, etc.; important Mn fertilizer, feed additive, for organic pigments, catalyst in H_2S oxidation.
Salts of Organic Acids	
Acetate	Oxidation catalyst in manufacture of dibasic acids (i.e. terephthalic, adipic acids) for synthetic fibers; also polymerization catalyst.
Acetylacetonate	Catalyst.
Ethylenebis (Dithiocarbamate) (Maneb)	Fungicide.
Gluconate	Feed and food additive; dietary supplement.
Glycerophosphate	Food additive, dietary supplement.
Lactate	Medicine.
Soaps	Driers in printing inks, paints and varnishes.
Mn chelates (complexes with EDTA, Lignosulfonates, dibasic sugar acids, gluconic acid)	liquid fertilizers, as feed and food additives.
Metalorganic Methylcyclopentadienyl-manganese tricarbonyl (MMT, C1-2)	Antiknock additive for motor fuels, combustion improver for heavy fuel oils.

TABLE IX

PRINCIPAL USES OF POTASSIUM PERMANGANATE

Category	Applications
Chemical Manufacture and Processing	
Organic Synthesis	Important industrial oxidant in the manufacture of chemical and pharmaceutical intermediates; also used as oxidation catalyst, e.g. in fatty acid production from paraffins.
Inorganic Manufacture	Mn catalysts, Purafil.
Purifying Agent	Organic compounds, mostly solvents.
Environmental	
Water	Potable: removal of Fe-Mn, taste and odor; control of trihalomethanes.
	Industrial and waste: removal of phenol and other organic contaminants; radioactive decontamination; clean-up of acid mine draining.
Air	Industrial effluents: removal of odorous constituents by wet scrubbing (rendering and roofing plants; foundries; food processing plants; sewage plants).
	Indoor spaces: odor control with Purafil (solid formulation containing $KMnO_4$).
Metal-Surface Treatment	Scale and smut removal from carbon steel and stainless steels.
Hydrometallurgical Uses	Purification of zinc sulfate solution in electrowinning of zinc; Fe-Mn removal from $ZnCl_2$ solns.
Miscellaneous	Bleaching of beeswax, jute fibers, clays; in fishery management for detoxification of fish poisons; alleviation of temporary oxygen depletion, control of fish parasites, etc.; as laboratory chemical in analytical and preparative organic chemistry.

2.1 Summary

All manganese ores are imported in North America and almost all are used in the metallurgical industry. Most manganese is used as ferromanganese in the steel industry for alloying to fix sulphur and to increase strength. Small amounts are used for alloying with aluminum. Manganese oxides are used mainly in dry-cell batteries and as colourant in brick and tile manufacture. Manganese chemicals such as permanganate are used as oxidants in the chemical and pharmaceutical industries and other chemicals are used in many industries such as textile, agriculture and food.

3. MANGANESE IN WASTE STREAMS

There are two types of waste materials; process slags from ferroalloy operations, and steelmaking slags. A summary of typical slag compositions from various origins is shown in Table X.

Standard ferromanganese slags of No. 1 and No. 2 composition are suitable for making silicomanganese. Thus, there is no real disposal problem. Composition No. 3 with 25% MnO approaches the low range of manganese contents reported for these slags (20 - 25% MnO)[1]. These slags are normally discarded and represent a potential source for recovery. This is also true for all silicomanganese slags.

Of the steelmaking slags, only the BOF slags are known to be recycled for recovery of lime and iron values.

4. CANADIAN MANUFACTURE OF MANGANESE PRODUCTS

4.1 Ferroalloys and Manganese Metal

Since manganese ores are not being mined domestically all requirements for metallurgical and non-metallurgical applications are imported.

Based on the information supplied by Statistics Canada and Energy, Mines and Resources Canada [8] as shown in Tables XI and XII, the domestic consumption of ferromanganese and silicomanganese is showing a downward trend. In 1970 consumption amounted to some 98,000 tonnes. In 1979 this figure dropped to 74,000 tonnes of alloy. The quantity of imported ferromanganese and silicomanganese, on the other hand, has increased from 19,000 tonnes in 1970 to 41,000 tonnes in 1975 and to 106,000 tonnes of alloy in 1979. This trend, if continued, represents a serious threat to the domestic ferroalloy producers.

TABLE X

TYPICAL SLAG COMPOSITION FOR POTENTIAL MANGANESE RECOVERY

	Std. Ferromanganese Slags			Silicomanganese Slags			BOF Slag	OH Run Off Slags		Electric Furnace Meld-Down Slag
	#1 Ref.(3)	#2 (10)	#3 (11)	#1 (10)	#2 (1)	#3 (1)	(12)	55% HM* (13)	70% HM (13)	(13)
MnO	38.7	33.4	(25)	12	16-18	5-10	5	21.6	15.8	12.7
SiO_2	24.7	22.4	(20)	39.2	42-45	34-45	12.8	26.4	19.2	13.4
Al_2O_3	14.4	(20)	(45)	(25)	(25)	(30)	.3	2.9	2.5	3.5
CaO	13.0	17.3	(10)	22.1	8-12	15-25	51.1	14.1	7.5	40.9
MgO	2.7	1.5			1.5		6.0	6.5	3.7	8.2
FeO					1-1.5		15.1	22.3	42.8	14.8
Fe_2O_3							8.4	3.0	4.6	-
P_2O_5							1.2	2.4	2.5	.6
S							.1	.08	.09	.1

* Hot Metal Composition (Typical): %C - 4.3, %Mn - 2.20, %Si - 1.34, %P .255, %S .03

TABLE XI

CANADA, MANGANESE, TRADE AND CONSUMPTION, 1978 AND 1979

	1978		1979[P]	
	(tonnes)	($)	(tonnes)	($)
Imports				
Manganese in ores and concentrates[1]				
French Africa, nes	-	-	18 935	2,970,000
United States	24 636	4,563,000	5 182	1,889,000
Brazil	38 756	6,415,000	10 996	1,832,000
Gabon	39 759	3,718,000	9 552	1,479,000
Other Countries	33 295	3,746,000	486	177,000
Total	136 446	18,442,000	45 151	8,347,000
Manganese metal				
South Africa	7 539	6,585,000	7 811	8,326,000
Other Countries	400	488,000	464	532,000
Total	7 939	7,073,000	8 275	8,858,000
Ferromanganese, including Spiegeleisen[2]				
South Africa	11 803	5,454,000	22 130	12,366,000
United States	5 864	3,300,000	19 480	11,800,000
Brazil	-	-	10 500	5,118,000
Portugal	6 957	4,635,000	8 892	4,445,000
Norway	-	-	5 043	3,307,000
India	-	-	5 726	2,462,000
United Kingdom	-	-	5 041	2,313,000
Netherlands	-	-	5 001	2,199,000
Other Countries	2 188	750,000	1 866	1,272,000
Total	26 812	14,139,000	83 679	45,282,000
Silicomanganese, including Silicospiegeleisen				
United States	6 309	2,902,000	12 079	7,054,000
Norway	5 779	2,412,000	6 776	3,551,000
Other Countries	3 754	1,864,000	3 021	1,741,000
Total	15 842	7,178,000	21 876	12,346,000
Exports				
Ferromanganese[2]				
United States	19 878	5,960,000	11 962	2,767,000
Jamaica	46	27,000	81	63,000
Total	19 924	5,987,000	12 043	2,830,000
Consumption				
Manganese Ore				
Metallurgical Grade	198 560	..	58 587	..
Battery and Chemical Grade	2 760	..	3 056	..
Total	201 320	..	61 643	..

Sources: Statistics Canada; Energy, Mines and Resources Canada

[1] Mn Content; [2] Gross Weight.

[P] Preliminary; - Nil; .. Not Available.

TABLE XII

CANADA, MANGANESE IMPORTS, EXPORTS AND CONSUMPTION,
1965, 1970, 1975-79

	Imports			Exports	Consumption	
	Manganese Ore[1]	Ferro-Manganese	Silico-Manganese	Ferro-Manganese	Ore	Ferromanganese and Silicomanganese
	(gross weight, tonnes)					
1965	81 175	31 354	714	3 463	108 217	70 186
1970	115 052	17 891	975	510	153 846	97 952
1975	69 773	35 701	5 732	1 168	160 976	95 869
1976	118 972	25 098	12 056	9 861	238 629	83 687
1977	57 644	29 404	4 835	23 104	182 157	82 467
1978	136 446	26 812	15 842	19 924	201 320	69 349
1979[P]	45 151	83 679	21 876	12 043	61 643	73 774

Sources: Energy, Mines and Resources Canada: Statistics Canada.

[1] Mn Content.

[P] Preliminary.

During 1978/1979 ores were being imported from Africa, Brazil and the U.S., ferromanganese and silicomanganese primarily from South Africa, and the U.S., Brazil, Portugal and Norway. Manganese metal came mainly from South Africa.

Union Carbide Canada Limited and Chromasco Limited maintain operating facilities at Beauharnois, Quebec, for smelting manganese ores.

While Union Carbide's U.S. ferroalloy plants have been purchased by Elkem Metals Company, Pittsburgh, Pa., Head Office, Elkem A/S, Oslo, Norway, the final purchase of the Metals business of Union Carbide Canada Limited has not taken place as yet. Elkem has an option to purchase Union Carbide Canada Limited's Metals plant at Beauharnois and Chicoutimi, Quebec through 1987.

The following is a summary of Union Carbide's operation and we are indebted to the Company for their permission to reproduce it here.

(a) Ore Source

Approximately 200,000 tons of ore are imported mainly from Brazil (Amapa Mine), South Africa (Associated Manganese Mines, S.A. and Adams, S.A.) as well as from Gabon (COMILOG).

The Brazilian metallurgical grade ore analyzes 48-49% Mn, 5-6% Fe, 4-6% Al_2O_3, 2-3% SiO_2, 0.09% P and 13.2% O_2. The carbonate ores from South Africa grade 38.5% Mn, 4.9% Fe, 0.024% P and 6% O_2. The Gabon ore contains on the average 50-52% Mn, 6-8% Al_2O_3, 1.5-3% SiO_2, 2.5-3% Fe, 0.11-0.13% P.

Current ore prices including transportation amount to approximately $100.00 per metric ton including transportation for Amapa and COMILOG ores. The carbonate ores range from $75 - 80/metric ton. Transportation charges are roughly $25/metric ton.

(b) Manganese Slag

Union Carbide has a stockpile of more than 100,000 tons manganese bearing process slag of various grades (25-35% Mn and 35-45% Mn). This material is sized -4 inch +3/8 inch and can be used as feed for the smelting operation. Some of the -3/8 inch slag is sold as flux to replace fluorspar. The slag is being stored at Beauharnois and Melocheville, Quebec.

(c) Operation

No. 18 furnace at Beauharnois, Quebec is capable of producing 120,000 tons/year of standard ferromanganese or 60,000 tons/year of silicomanganese at power inputs of 33-35 MW. The furnace is of Japanese design and is operated in conjunction with an ore preparation plant to produce ore sinter as furnace feed.

(d) Standard Ferromanganese Price Trend

1950	$ 173/ton alloy	)
1957	280	)
1963	174	)
1972	186	)
1974	230-390	) Canadian $ per Gross Ton
1975	440	)
1976	415	)
1978	465	)

Metric Conversion:

January 1, 1981

1982 $ 556/ton alloy - Canadian $ per Metric Ton

(e) Current Alloy Prices (first quarter 1982)

Standard Ferromanganese	$556/MT alloy, lump, bulk, f.o.b. Beauharnois
Low Carbon Ferromanganese	$ 1.808/kg Mn (87% Mn - 1%C)
Medium Carbon Ferromanganese	$ 1.289/kg Mn (1.5% C Max.)
Electrolytic Manganese (Elmang)	$ 2.188/kg Mn
Silicomanganese	$ 0.6945/kg alloy

(f) Domestic Sales

Standard Ferromanganese	50,000 metric tonnes per year
Silicomanganese	16,000 metric tonnes per year

(g) Customers

Stelco, Dofasco, Algoma, Sidbec-Dosco, Sydney Steel, Ipsco, Lasco and Steel Foundries.

(h) Strategy in Case of Non-Supply of Mn Ore

Short term - Depend on U.S. stockpiles
Medium term - Silicomanganese production from slag pile
Long term - Shut-down of operation

Electrolytic manganese metal is not being produced in Canada. Imported metal comes mainly from South Africa. The producers of Mn metal in the U.S. include:

Metals Division of Union Carbide Corporation
Foote Mineral Co.
Kerr - McGee Chemical Corporation

4.2 Manganese Oxides and Chemicals

No Synthetic Manganese Dioxide and Manganese Chemicals such as potassium permanganate are reported as being produced in Canada.

4.3 Summary

All manganese ore requirements for metallurgical and non-metallurgical applications are imported. The quantity of imported ferromanganese and silicomanganese is increasing while importation of ore is decreasing. The ore comes mainly from Africa, Brazil, Gabon and U.S. while manganese metal comes mainly from South Africa. Ferromanganese and silicomanganese comes from South Africa, U.S., Brazil, Norway and Portugal. Union Carbide Canada Ltd. and Chromasco Ltd. are the main Canadian smelters of manganese ores in Canada. No manganese chemicals are being produced in Canada.

5. CANADIAN USERS OF MANGANESE PRODUCTS

5.1 Ferroalloys and Manganese Metal

By far the greatest user of ferromanganese and silicomanganese is the steel industry. Canadian raw steel output in 1981 was 14.8 million MT, down from 15.9 million MT a year earlier.[14] Canada ranks No. 11 among the steel producing nations (see Table XIII). Table VI shows specific manganese requirements for various types of steel to impart hardness, toughness, hardenability and wear resistance.

It is interesting to note that a number of iron ores for use in blast furnaces at Dofasco, Stelco and Algoma for instance, contain high manganese levels. Compositions of typical ores [15] are shown in Table XIV,

Approximately 80% of the manganese values is found in the hot metal and 20% in the blast furnace slag. The manganese level in the hot metal is controlled at Stelco to approximately 1% Mn by blending suitable iron ores.

The hot metal is blown in the BOF furnace with oxygen and suitable fluxes employing steel scrap and iron ore as coolants. The resulting steel contains 0.1 to 0.2% Mn and the BOF slag 5-8% MnO along with 50% lime and iron oxides equivalent to 25% Fe. Recovery of manganese into the slag amounts to approximately 80%. A material balance for oxidation of one metric tonne of hot metal [16] is shown in Table XV.

Both Stelco and Dofasco are sending the BOF slag to Heckett Engineering for processing. The +4 inch magnetics are returned to the BOF shop as scrap, the -4 inch +3/8 inch magnetic fraction is returned to the blast furnece for its iron values. The +3/8 inch non-mags are returned to the blast furnace as well for its lime and iron units. The -3/8 inch slag is stockpiled for discard or miscellaneous used including land fill.

TABLE XIII

RAW STEEL OUTPUT (24)

NATION	1981 (est)	1980	1976
USSR	150.0	147.9	144.8
USA	108.5	101.7	116.1
JAPAN	101.7	111.4	107.4
WEST GERMANY	41.9	43.8	42.4
CHINA	38.0	37.1	20.5
ITALY	24.5	26.5	23.5
FRANCE	21.0	23.2	23.2
POLAND	17.5	19.5	15.6
UNITED KINGDOM	15.7	11.3	22.3
CZECHOSLOVAKIA	15.5	14.9	14.7
CANADA	14.8	15.9	13.3
ROMANIA	13.5	13.2	11.0
BRAZIL	13.1	15.3	9.3
SPAIN	12.9	12.7	11.0
BELGIUM	12.3	12.3	12.1
SOUTH KOREA	10.7	8.6	3.5
INDIA	10.5	9.5	9.4
SOUTH AFRICA	9.1	9.1	7.1
AUSTRALIA	7.6	7.6	7.8
MEXICO	7.6	7.1	5.3
EAST GERMANY	7.4	7.3	6.7
NORTH KOREA	6.0	5.8	3.0
NETHERLANDS	5.5	5.3	5.2
AUSTRIA	4.6	4.6	4.5
YUGOSLAVIA	4.0	3.6	2.8
LUXEMBOURG	3.8	4.6	4.6
SWEDEN	3.8	4.2	5.1
HUNGARY	3.7	3.8	3.7
TAIWAN	3.2	4.2	1.6
ARGENTINA	2.6	2.7	2.4
BULGARIA	2.6	2.6	2.5
FINLAND	2.4	2.5	1.6
TURKEY	2.4	2.5	2.0
VENEZUELA	2.1	1.8	0.9
OTHERS	12.4	13.4	9.2
TOTAL:	712.9	717.5	676.1

TABLE XIV

Manganese Bearing Iron Ores
Typical Composition

GRADE NAME	%Fe	Mn	P	S	SiO_2	Al_2O_3	CaO	MgO
Algoma Sinter Superfluxed	47.23	2.60	.025	0.102	9.33	1.22	11.56	7.29
Wabush Pellets	63.70	1.91	0.009	0.005	3.05	0.27	0.13	0.04
Knob Pellets	62.62	0.42	0.043	0.006	5.08	0.90	0.39	0.04

TABLE XV

MATERIAL BALANCE FOR OXIDATION OF ONE METRIC TON OF HOT METAL

INPUT			OUTPUT	
HOT METAL			**STEEL**	
Fe		939.65 kg	Fe	908.38 kg
C		44.30	C	1.82
Si		8.00	Si	0.00
Mn		7.00	Mn	1.37
P		0.80	P	0.09
S		0.25	S	0.15
O		0.00	O	0.27
		1000.00		912.08
FLUX			**SLAG**	
High-calcium lime		63.02	SiO_2	17.89
Dolomitic lime		19.61	CaO	71.42
			CaS (S 0.10)	0.23
CaO	71.60		MgO	8.59
MgO	8.59		MnO	7.27
SiO_2	0.78		P_2O_5	1.62
Fe_2O_3	0.16		FeO	21.29
Al_2O_3	0.40		Fe_2O_3 (Total Fe 24.81)	11.81
L.O.I	1.10		Al_2O_3	0.40
	82.63			140.52
GASEOUS OXYGEN	59.97 NM^3		**FUME**	
O_2		85.20	Fe_2O_3	9.40
N_2 + A		0.37	**GAS**	
		85.57	N_2	0.37
			CO	89.16
			CO_2	15.57
			L.O.I.	1.10
				106.20
TOTAL INPUT		1168.20	**TOTAL OUTPUT**	1168.20

Atlas Steels Company presently consumes approximately 1,700 tons/year of standard ferromanganese, 350 tons/year of M.C. ferromanganese and 100 tons/year of electrolytic manganese for the production of approximately 210 tons of stainless, high alloy and low alloy steel grades.

Hadfield manganese steel (10-14% Mn,1.0-1.4% C) has excellent work hardening properties and is used for making components subjected to sever impact and abrasion. It is produced in open-hearth, electric-arc and induction furnaces. Manganese is added as high,medium and low-carbon ferromanganese.

In Canada:

Hadfield steel is produced by:
Fahramet, Orillia, Ontario
Black Clawson Kennedy, Owen Sound, Ontario
Welmet Industries, Welland, Ontario
Esco, Port Hope, Ontario
Esco, Port Coquitlan, B. C.
Griffin Canada Inc., St. Hyacinthe, Quebec
Abex Industries, Joliette, Quebec
Abex Industries, Selkirk, Manitoba
Marine Industries, Sorel, Quebec

Fahramet has an annual usage (1981) of 75 tons of standard ferromanganese, 27 tons of medium-carbon ferromanganese and 7.5 tons of low-carbon material. Esco consumed 207 tons of ferromanganese and 126 tons of silicomanganese in 1981.

Neither Fahramet nor Esco are worried about short supply situations regarding manganese. Esco is more concerned about chromium supplies.

5.2 Wrought and Cast Aluminum Products

Manganese/aluminum master alloys are being manufactured by Shieldalloy Corporation in the U.S. and imported, most likely through Metallurg (Canada) Ltd. These alloys are available containing 20, 25 or 30% manganese, balance aluminum. Residual elements are limited to 0.20% Fe, 0.15% Si and 0.02% each of Ti, V, Cr, Mg, Cu, Ni, Zn and Zr. Boron is kept to 0.01%.

Union Carbide Canada Ltd. markets a briquet containing 75% electrolytic manganese -25% aluminum featuring fast dissolution into the aluminum bath. Reynolds Aluminum is said to import a considerable quantity of electrolytic manganese from South Africa (Delta Manganese) for making their own master alloys.

Casting alloy grades, typically contain 0.3% Mn (ASTM SC 82A) or 0.7% Mn (ASTM SC 122A). Wrought alloy grades contain up to 1% Mn (5000 series) and up to 1.5% Mn in the 3000 series material. Usually, aluminum sheet scrap of the 3,000 series variety is in fair abundance. This often creates a problem of too high a manganese level in the feed stocks relative to the manganese content in the finished product.

5.3 Battery-Grade Manganese Oxide

Duracell, Union Carbide and Ray-O-Vac are the three competitors in the Canadian battery scene. However, supplies of electrolytic manganese dioxide are being imported from the U.S:

Kerr McGee, Henderson, Nevada
Electric Storage Battery Inc., Covington, Tenn.
and Japan:
Toyo Soda Manufacturing Co. Ltd., Hyuga, Japan
via Mitsubishi Distributors.

Union Carbide estimates usage of 1000 MT/year and Duracell forsees a usage of 2200 MT/year. These two battery manufacturers are not concerned about short supply of manganese dioxide.

Union Carbide rely on a New York buyer who purchases EMD from all over the world with the bulk of the use coming from South Africa.

5.4 Summary

The largest user of ferromanganese and silicomanganese in Canada is the steel industry. Manganese is required to improve the properties of various types of steels. There are several Canadian companies producing Hadfield Steel used for its impact and abrasion resistance. None of these companies appear to be worried about short supply.

In the aluminum industry, manganese is used as an alloy constituent the higher manganese contents being in the wrought alloy grades. In the lower manganese grades there is a problem of balancing scrap to attain the low values of manganese required.

All the battery grade manganese dioxide is being imported monthly from the U.S. The battery manufacturers contacted were not concerned about a short supply of manganese dioxide.

6. FOREIGN OPERATIONS

The United States consumption of ferromanganese over the last five years is shown in Table XVI and compared with imported ferromanganese. Again, there is a trend towards reduced tonnage of imported ores and increased tonnages of imported alloys. In fact, 60% of the ferromanganese consumed in 1977 was imported. This percentage has increased to 85% in 1981 [17], and amounted to 740,000 tonnes of alloys.

The changes in ownership of the U.S. electric-furnace ferroalloy plants put U.S. production of manganese ferroalloys predominantly under foreign control.

The Japanese ferroalloy producers have a combined production capacity of over 1.5 MM tonnes of manganese ferroalloys to meet domestic steel production requirements of up to 140 million tons. [18]. In 1979 steel production was in the order of 110 million tons. No alloys from South Africa are being imported because of the strong position of the Japanese Mn-ore buyers. [18].

7. WORLD SUPPLY POTENTIAL

7.1 Manganese Ores

Total land-based world manganese reserves are estimated to be $3,100 \cdot 10^6$ metric tonnes contained manganese. The total seabed nodules are approximately 5 times larger ($16,000 \cdot 10^6$ metric tonnes contained Manganese).

According to Table XVII, the Republic of South Africa and the USSR own more than 80% of the land-based reserves. The North American share amounts to only $98 \cdot 10^6$ tonnes Mn or 3.2% and includes:

TABLE XVI

UNITED STATES: IMPORTS, EXPORTS, CONSUMPTION[17] 1981

	(Thousand Short Tons - Gross Weight)				
	1977	1978	1979	1980	1981 (est.)
Imports - Manganese Ore	931	548	500	698	550
- Ferromanganese	534	680	821	606	740
Exports - Manganese Ore	138	200	58	53	80
- Ferromanganese	6	9	25	12	18
Shipments from Govt. Stockpile					
- Manganese	821	632	607	366	315
- Ferromanganese	-	-	-	-	-
Reported Consumption					
- Manganese Ore	1359	1281	1372	1071	1075
- Ferromanganese	886	985	976	789	885

TABLE XVII

IDENTIFIED WORLD MANGANESE RESOURCES
(10^6 METRIC TONS MANGANESE CONTENT)

	Reserves[a]	Other[b]	Total	Percentage of world reserves
North America				
United States				
Arizona		6.2	6.2	
Arkansas		7.1	7.1	
Colorado		3.4	3.4	
Maine		30.3	30.3	
Minnesota		19.8	19.8	
Total United States		66.8	66.8	2.2
Canada		15.9	15.9	0.5
Mexico	4.1	11.4	15.5	0.5
Total North America	4.1	94.1	98.2	3.2
South America				
Bolivia		4.5	4.5	
Brazil	39.6	23.6	63.2	2
Chile	0.4		0.4	
Total South America	40.0	28.1	68.1	
Europe				
Bulgaria	4.1		4.1	
Greece	0.21		0.21	
Hungary	0.24		0.24	
USSR	634.9	544.2	1,179.1	38
Total Europe	639.45	544.2	1,186.65	
Africa				
Gabon	77.1		77.1	2.5
Ghana	5.99	9.1	15.09	
Ivory Coast		1.4	1.4	
Morocco	0.43		0.43	
Republic of South Africa	716.5	708.0	1,424.5	46
Upper Volta		9.1	9.1	
Zaire	3.08	1.0	4.08	
Total Africa	803.1	728.6	1,531.7	
Asia				
People's Republic of China	15.4	15.4	30.8	
India	25.4	10.9	36.3	
Japan	0.7		0.7	
Thailand	1.2	2.5	3.7	
Total Asia	42.7	28.8	71.5	
Oceania				
Australia	145.1	13.6	158.7	5
Fiji	0.07	0.27	0.34	
New Hebrides	0.07		0.07	
Total Oceania	145.24	13.87	159.11	
WORLD TOTAL - LAND[c]	1,700	1,400.0	3,100.0	
WORLD TOTAL - SEABED NODULES[d]		16,000.0	16,000.0	

[a] Commercial grade.
[b] Low grade.
[c] Rounded.
[d] Estimated.

U.S.A.	$66.8 \cdot 10^6$ tonnes Mn
Mexico	$15.5 \cdot 10^6$ tonnes Mn
Canada	$15.9 \cdot 10^6$ tonnes Mn
Total North America	$98.2 \cdot 10^6$ tonnes contained Mn

It is noteworthy that most North American manganese deposits contain low grade ores which cannot be readily used for smelting standard ferromanganese.

World manganese occurances are shown in Figure 3 on a global basis.

Based on 1977 information [10, 19] major ore suppliers are the USSR, South Africa, Gabon, India and Australia. A listing is shown in Table XVIII. Imported ore compositions are listed in Table XIX and a price comparison of Mn ores for the period 1954 - 1978 is given in Table XX.

Manganese mine operations are summarized in reference (10) and described in detail in the 1980 Ferro Alloy Manual [18] and include Groote Eylandt in Australia, South African Mines operated by Amcor Ltd. and Anglo American Corporation, Molango in Mexico, Amapa in Brazil, and Moanda in Gabon.

7.2 Seabed Nodules

The contained manganese values in seabed nodules exceeds land-based manganese occurrences by a factor of 5, totalling 16 billion tonnes contained Mn [19].

Figure 3 - World Manganese Sources

TABLE XVIII

PRODUCTION OF ORE BY PRINICPAL COUNTRIES
THOUSAND METRIC TONS

Reference (6)

Country	Mn, %	1973	1974	1975	1976	1977
USSR	35	8230	8155	8459	8636	8500
South Africa	>30	4168	4745	5770	5452	5048
Gabon	50-53	1915	2064	2064	2217	1851
India	10-54	1532	1502	1577	1760	1774
Australia	37-53	1520	1522	1555	2154	1387
China	>30	998	998	998	998	998
Brazil	38-50	2153	1788	2156	1696	898
Ghana	30-50	318	250	409	312	267
Morocco	50-53	146	175	131	117	114

TABLE XIX

CHEMICAL COMPOSITION OF IMPORTANT MANGANESE ORES, % DRY BASIS[a]

Reference (3)

Location	Typical Moisture	Mn	Fe	SiO_2	Al_2O_3	CaO	MgO	BaO	P	As	K_2O	CO_2	Available Oxygen [b]
Amapa, Brazil	4.8	48.2	6.2	3.4	5.0	0.11	0.05	0.18	0.09	0.17	1.6	0.04	12.9
Moanda, Gabon	5.2	51.4	2.6	2.6	6.1	0.08	0.06	0.21	0.11	0.01	0.72	0.07	14.1
Groote Eylandt, Australia	3.9	49.5	3.6	6.1	4.8	0.06	0.08	0.45	0.07	0.01	1.5	0.02	13.6
South Africa,													
Mamatwan	1.6	38.4	5.0	4.2	0.4	13.4	3.3	0.02	0.02	0.00	0.03	13.8	5.6
Wessels	1.3	47.0	13.2	4.9	3.2	4.1	0.74	0.36	0.04	0.00	0.12	1.7	6.3
Molango[c], Mexico	0.2	38.8	8.1	14.2	3.2	8.5	10.6	0.01	0.07	0.01	0.03	0.15	0.1
Nikopol, USSR	6.9	44.8	1.8	12.8	1.9	1.7	1.6	0.46	0.21		1.2	1.5	10.2

[a] Ore Analyses by Union Carbide.

[b] Associated with Mn in excess of MnO.

[c] Calcined nodules.

TABLE XX

PRICE DEVELOPMENT OF MANGANESE ORE, $/METRIC TON UNIT[a]

Year	Reference (6) Actual Price	1977 Dollars Basis
1954	0.94	2.24
1956	1.43	3.23
1958	1.19	2.54
1960	0.92	1.90
1962	0.89	1.80
1964	0.67	1.31
1966	0.74	1.37
1968	0.59	1.01
1970	0.53	0.82
1972	0.59	0.83
1974	0.88	1.08
1976	1.42	1.51
1978	1.37	1.28

[a] To obtain the price per metric ton of ore, multiply the metric ton unit price by the percent manganese content.

Average wet concentration of nodules in the Pacific is 10 kg/m^2 with 7 kg/m^2 being the lower economical limit [21]. The belt of nodules off the Pacific coasts of North and South America are rich in manganese with nodule concentrations of 24 to 33 kg/m^2.

Average concentrations of metals in nodules for different oceans [22] and for different areas within the Pacific Ocean [23] are shown in Tables XXI and XXII.

Extraction of nickel, copper, cobalt and manganese values by hydrometallurgical means is the most likely technique to be used. Selective dissolution of copper, nickel and cobalt with dilute sulphuric acid tend to yield low metal recoveries. These can be improved by using higher temperatures and/or lower pH levels at the expense of selectivity. Autoclave leaching improves rates of dissolution at high selectivity with respect to iron and manganese.

The Hydrochlorination process [24] as developed by Deepsea Ventures Inc. dissolves all metal values including manganese. Individual metals are separated and recovered by ion exchange or solvent extraction followed by electrowinning. Recoveries of values by this method range from 93-96%. Figure 4 shows the Deepsea Venture Flowsheet.

Reduction roasting with No. 6 fuel oil at 600 to 800°C followed by ammonical leaching will extract 95% of copper and nickel with cobalt extraction of 85% [25].

Companies and consortia involved in developing ocan mining methods include:

TABLE XXI

AVERAGE CONCENTRATIONS OF METALS IN FERROMANGANESE NODULES AND CRUSTS IN DIFFERENT OCEANS (AFTER HORN, HORN, AND DELACH)

	Metal Concentration, %				
	Ni	Cu	Co	Mn	Ca
North Atlantic					
Kelvin Seamounts	0,11	0,04	0,04	1,80	
Blake Plateau	0,52	0,08	0,42	14,7	10,2
Abyssal Hills	0,41	0,29	0,40	14,9	
Mid-Atlantic Ridge	0,18	0,12	0,3	10,4	
South Atlantic					
Rio Grande Rise and adjacent plain	0,14	0,09	0,05	7,2	
Agulhas Plateau	0,83	0,15	0,36	17,1	1,2
Adjacent deep	0,67	0,16	0,18	13,0	
Indian Ocean					
Madagascar Basin	0,24	0,12	0,25	11,0	
Kerguelen-Gaussberg Ridge	0,34	0,05	0,04	2,3	
Crozet Basin	0,42	0,12	0,14	12,4	
South Pacific					
Deep	0,13	0,10	0,31	11,36	
Manihiki Plateau	0,30	0,17	0,51	16,9	

TABLE XXII

AVERAGE COMPOSITION* OF SURFACE NODULES FROM DIFFERENT AREAS WITHIN THE PACIFIC OCEAN (AFTER CRONAN)

	1	2	3	4	5	6	7	8	9
Mn	15,85	33,98	22,33	19,81	15,71	16,61	16,87	13,96	12,29
Fe	12,22	1,62	9,44	10,20	9,06	13,92	13,30	13,10	12,00
Ni	0,348	0,097	1,080	0,961	0,956	0,433	0,564	0,393	0,422
Co	0,514	0,00075	0,192	0,164	0,213	0,595	0,395	1,127	0,144
Cu	0,077	0,065	0,627	0,311	0,711	0,185	0,393	0,061	0,294
Pb	0,085	0,006	0,028	0,030	0,049	0,073	0,034	0,174	0,015
Ba	0,306	0,171	0,381	0,145	0,155	0,230	0,152	0,274	0,196
Mo	0,040	0,072	0,047	0,037	0,041	0,035	0,037	0,042	0,018
V	0,065	0,031	0,041	0,031	0,036	0,050	0,044	0,054	0,037
Cr	0,0051	0,0019	0,0007	0,0005	0,0012	0,0007	0,0007	0,0011	0,004
Ti	0,489	0,060	0,425	0,467	0,561	1,007	0,810	0,773	0,634
L.O.I.**	24,78	21,96	24,75	27,21	22,12	28,73	25,50	30,87	22,52
Depth,m	1146	3003	4537	4324	5049	3539	5001	1757	4990

* In air-dried mass per cent.
** Loss on ignition.

1 Southern Borderland Seamount Province
2 Continental Borderland off Baja California
3 North-east Pacific
4 South-east Pacific
5 Central Pacific
6 South Pacific
7 West Pacific
8 Mid-Pacific Mountains
9 North Pacific

Energy Mines & Resources Canada
FINAL REPORT
Contract No. 77001

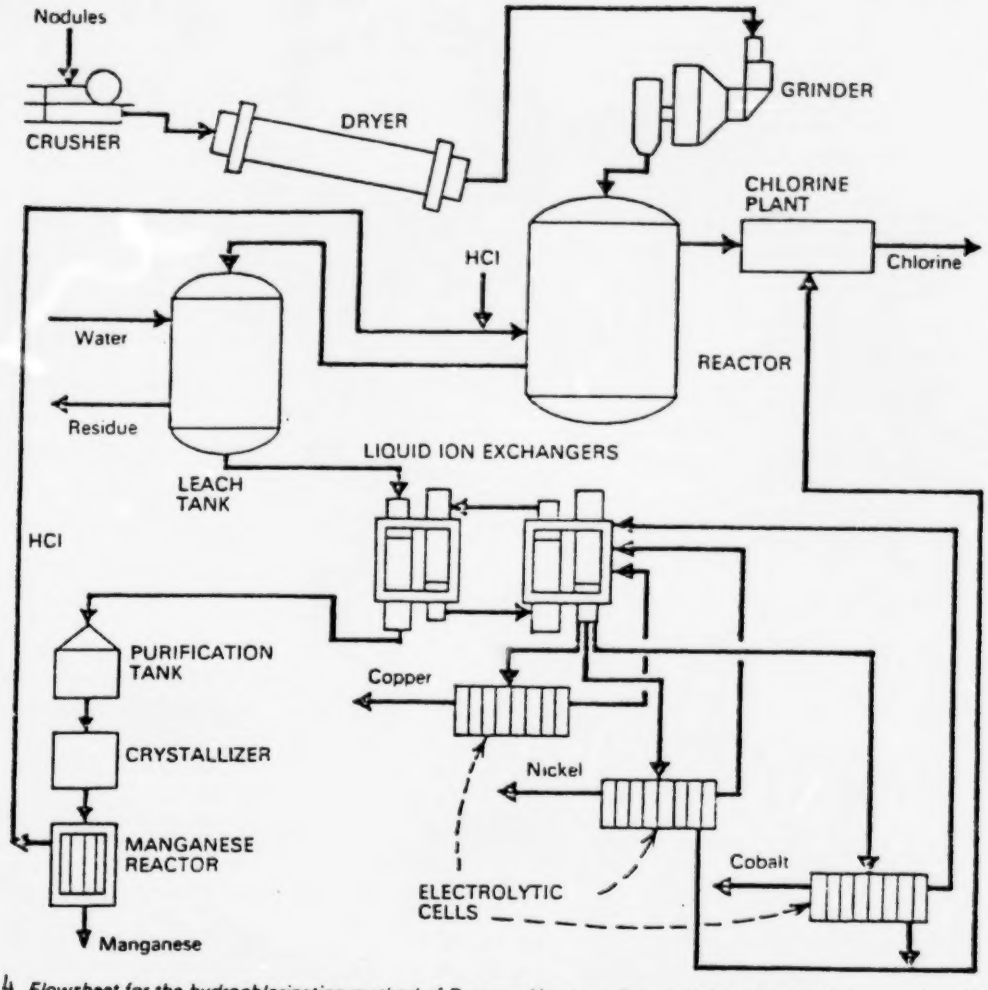


FIGURE 4 Flowsheet for the hydrochlorination method of Deepsea Ventures, Inc., (adapted from N.R. Iammartino. Metals from nodules. Chem. Engng (Albany). 25th Nov., 1974. pp. 52-53).

- Summa Corp. (Howard Hughes) operated 26,000 ton prototype ocean mining ship (Glomar Explorer)
- Kennecott, Rio Tinto, Consolidated Gold Fields, Mitsubishi, Noranda. Mining and processing research at San Diego.
- Deep Sea Ventures Inc., Ocean Mining Associates, Union Miniére Nichimen Co., Itoh and Co., Kanematsu-Gosho, Ltd. and U.S. Steel.
- German consortium (A.M.R.)
- French consortium CNEXCO, Le Nickel
- International Nickel Co.
- Japanese Companies
- U.S.S.R.

7.3 Ferromanganese Alloys and Manganese Metal

On a world-wide basis, excluding U.S.S.R. and China, there are 80 companies in 21 countries producing manganese metal and/or manganese bearing ferroalloys [20]. A listing of these companies is shown in Table XXIII. Free World capacities (1979) for various products are:

Standard Ferromanganese	4.17 million	tonnes alloy/year
M.C. Ferromanganese	250,000	tonnes alloy/year
L.C. Ferromanganese	22,000	tonnes alloy/year
Silicomanganese	1.46 million	tonnes alloy/year
Manganese Metal	62,000	tonnes metal/year

TABLE XXIII

WORLD PRODUCTION DIRECTORY, 1979 (CAPACITIES IN ANNUAL TONNES)

	HC FeMn	MC FeMn	LC FeMn	SiMn	Mn Metal
ARGENTINA					
Electrometalurgica Andina	10,000	-	-	2,000	-
Carbometal	10,000	-	1,000	-	-
Grassi	20,000	-	-	-	-
AUSTRALIA					
Tasmanian Electro	135,000	-	-	-	-
BELGIUM					
Sadacem	150,000	30,000		50,000	-
BRAZIL					
Alcan Aluminio	10,000	-	-	15,000	-
CSN	17,000	-	-	-	-
Paulista de Ferro-Ligas	-	44,000	-	17,000	-
Prometal	-	9,000	600	9,600	-
Sibra	90,000	8,000	-	35,000	-
CANADA					
Chromasco	25,000	-	-	25,000	-
Union Carbide Canada	65,000	-	-	25,000	-
CHILE					
Carburo y Metalurgia	1,000	-	-	1,000	-
Manganesos Atacama	4,000	-	-	-	-
FRANCE					
Bozel	-	-	-	*	-
Acieries de Paris & d'Outreau	450,000	-	-	50,000	-
Pompey	100,000	-	-	-	-
Sofrem	-	50,000		10,000	-
Universelle d'Acetylene et d'Electrometallurgie	30,000	-	-	10,000	-
WEST GERMANY					
GFE	-	35,000		-	-
Peine-Salzgitter	10,000	-	-	-	-
Hermann C. Starck	-	-	*	-	-
Thyssen	288,000	-	-	-	-
INDIA					
Dandeli Ferro-Alloys	12,000	3,000		6,000	-
Ferro-Alloys Corp.	40,000	-	-	5,000	-
Jeypore Sugar	24,000	-	-	-	-
Khandelwal Ferro-Alloys	40,000	-	-	-	-
Maharashtra Electrosmelt	50,000	-	-	-	-
Tata Iron & Steel	30,000	-	-	-	-
Universal Ferro & Allied Chemicals	36,000	-	-	-	-
Visvesvaraya Iron & Steel	3,000	-	-	2,000	-
ITALY					
Elettrosiderugica Italiana	60,000	-	-	-	-
Fucinati	25,000	-	-	-	-
Italghisa	40,000	-	-	-	-
Italsider	-	-	5,000	-	-
Carlo Tassara	5,000	15,000	-	4,000	-

TABLE XXIII (Cont'd)

WORLD PRODUCTION DIRECTORY, 1979

	HC FeMn	MC FeMn	LC FeMn	SiMn	Mn Metal
JAPAN					
Chuo Denki Kogyo	90,000	-	-	60,000	-
Furukawa Kogyo	*	*	*	*	-
Japan Metals & Chemicals	159,100	85,500		162,000	-
Kobe Steel	50,000	26,000	-	60,000	-
Minami Kyushu Kagaku	-	15,000		21,000	-
Mizushima Ferro-Alloy	153,000	-	-	71,400	-
Nippon Denko	100,000	24,000		95,000	-
Nippon Kokan	100,000	40,000	-	140,000	-
Pacific Metals	38,700	12,320	-	22,800	-
Toyo Menka Kogyo	10,000	-	-	3,000	-
Toyo Soda Mfg.	-	-	-	-	6,000
MEXICO					
Minera Autlan	115,000	-	-	-	-
Ferroalaciones de Mexico	20,000	-	-	-	-
NORWAY					
Elkem-Spigerverket	120,000	10,000	-	50,000	-
Sauda Smelteverk	170,000	40,000	5,000	60,000	-
Tinfos Jernverk	80,000	-	-	110,000	-
PERU					
Electrometalurgica Nacional	3,600	-	-	-	-
PHILLIPPINES					
Ferro-Chemicals	*	*	*	-	-
PORTUGAL					
Eurominas	150,000	-	-	-	-
SOUTH AFRICA					
Delta Manganese	-	-	-	-	28,000
Electrolytic Metal	-	-	-	-	16,790
Feralloys	100,000	-	-	-	-
Samancor	393,000	-	-	52,000	-
Transalloys	-	10,000	-	70,000	-
SPAIN					
Espanola de Carburos	40,000	-	-	20,000	-
Espanola de Fundiciones Electricos	*	*	*	-	-
Ferroaleaciones y Electrometales	-	-	10,000	-	-
Hidro Nitro	-	35,000		45,000	-
Sinosa	*	-	-	-	-
SWEDEN					
Airco Alloys	-	-	-	16,000	-
TAIWAN					
Tung Chou Industrial	*	*	*	3,000	-
UNITED KINGDOM					
BSC	80,000	-	-	-	-
Murex	-	-	300	-	-
UNITED STATES					
Airco Alloys	100,000	-	-	40,000	-
Chemetals Corp	-	25,000	-	-	*
Foote Minerals Co.	-	-	-	-	11,000
Kerr-McGee	-	-	-	-	*
Namco	-	*	*	*	-
Ohio Ferro-Alloys	50,000	-	-	20,000	-
Roane Electric	73,000	11,000	-	35,000	-
Tenn-Tex Alloy	30,000		-	30,000	-
Union Carbide	*	*	*	*	*
United States Steel	150,000	-	-	-	-

7.4 Manganese Dioxide

International Producers of Chemical and Electrolytic Manganese Dioxide are listed in Tables XXIV and XXV.

There are nine producers of CMD in the U.S. and Europe with a combined annual capacity of approximately 37,000 tonnes according to reference (6) and approximately 12 producers of EMD located in Japan, Greece, Ireland, the United States, India, West Germany, and Spain with total world capacity of 115,000 tonnes of product/year.

Analyses of Manganese ores for non-metallurgical applications are compiled in Table XXVI.

World and U.S. production capacities and 1979 prices for manganese oxides and chemicals as well as U.S. manufacturers are listed (6) in Table XXVII

7.5 U.S. Stockpile Inventory

The stockpile inventory as of March 31, 1981, of manganese related combined commodities was listed (26) as follows:

	Inventory	Goal
Standard ferromanganese	599,978	439,000 ST
M. C. ferromanganese	28,290	- ST
Ferromanganese-silicon	23,574	- ST
Electrolytic Manganese	14,172	- ST
Manganese ore - metallurgical	2,409,377	2,700,000 SDT
Manganese dioxide - battery grade	190,864	62,000 SDT
Manganese-chemical	220,955	170,000 SDT

ST = Short Ton

SDT = Short Ton, Dry Basis

No such inventories are being maintained in Canada.

TABLE XXIV

PRODUCERS OF CHEMICAL MANGANESE DIOXIDE (CMD)

Company	Location	Grade, Type, or Tradename	Capacity, t/yr	Applications	Remarks
Sedema	Tertre, Belgium	Faradiser M	23,000	Batteries	
Chemetals Corporation	Baltimore, Md.	Farsdiser M			
Chemetals Corporation	Baltimore, Md.	HP		Ferrites, high-purity lower oxides	
Chemetals Corporation	Baltimore, Md.	OG	8,600	Organic Oxidation	Typically contains 91% MnO_2, 2% H_2O
Chemetals Corporation	Baltimore, Md.	PG		Curing of Polymer Sealants[a]	Typically contains 76% MnO_2, 10% H_2O
Chemetals Corporation	Baltimore, Md.	WS		Batteries	92.6% MnO_2
Les Piles Wonder	Saint-Quen, Fr.	Philodyne-Ergogene	4,000	Batteries	Chemically activated natural battery ore
The Boots Co. Ltd.	Nottingham, UK.	Hydrated Manganese Dioxide	1,000	Batteries	From Saccharin manufacture
VEB Chemiekombinat	Bitterfield,GDR	Manganit[b]		Batteries	From Saccharin manufacture
Perstorp Austria GmbH	Vienna, Austria	Permanox		Batteries	From Saccharin manufacture
Shepherd Chemical Co.	Cincinnati, Ohio	808	300[c]	Curing of Polymer Sealants[b]	
General Metallic Oxides	Jersey City, N.J.		500[c]	Batteries	
Winthrop Laboratories	New York, N.Y.	Activated MnO_2		Organic Oxidations	$30/kg in 25-kg lots or larger

[a] Polysulfide rubber

[b] Also manufactured in Czechoslovakia

[c] Estimated

TABLE XXV

PRODUCERS OF ELECTROLYTIC MANGANESE DIOXIDE (EMD)

Company	Location	Product Capacity, t/yr	Grades	Year Installed: Remarks
Japanese or Japanese Owned:				
Toyo Soda Mfg. Co. Ltd.	Hyuga, Japan	18,000	Battery, Ferrite	1965
Tekkosha Hellas S.A.I. (joint venture Toyo Soda and Mitsubishi)	Thessaloniki, Greece	12,000	Battery	1975
Mitsui Mining and Smelting Co. Ltd.	Takehara, Japan	18,000	Battery, Ferrite	
Mitsui Denman	Little Island, Ireland	12,000	Battery	1976
Daiichi Carbon Co. Ltd.	Yokohama, Japan	4,200	Battery, Ferrite	1960's
U.S. or U.S. Owned:				
Kerr McGee	Henderson, Nev.	12,000	Battery	
Union Carbide	Marietta, Ohio	6,000	Battery	1968; entire production used captively
Union Carbide	Thana, nr. Bombay, Ind.	4,000	Battery	
Cia Nacional de Grafita S.A. (affiliate of Union Carbide)	Brazil	4,000	Battery	
Electric Storage Battery, Inc.	Covington, Tenn.	4,000	Battery	
Misc. Ownership:				
Hoechst A.G.	Knapsack, Cologne, FRG	12,000	Battery	1968; capacity increased from 8,000-12,000 t/yr in 1979
Cegasa S.A.	Vittoria,nr. Barcelona, Spain	4,000	Battery	
Several smaller plants: China, India, various COMECON countries		5,000		
WORLD TOTAL		115,000		

TABLE XXVI

ANALYSES OF MANGANESE ORES[a]
USED IN NONMETALLURGICAL APPLICATIONS OR MANUFACTURE OF Mn CHEMICALS, WT. %

Reference (6)

Constituent	1	2	3	4	5	6	7
Mn (total)	55.42	54.85	51.4	52.30	48.85	30.81	30-35
MnO_2	85.9	83.64	74.0	78.30	70.99	nil	
MnO	1.51	3.04	5.99	3.62	5.16	39.77	
Fe (total)	0.53					1.04	2-3
Fe_2O_3	0.76	2.64	3.16	3.13	7.55		
S	0.012	0.101		0.006		0.04	
P	0.039	0.08	0.140	0.095	0.081	0.06	
Cu	0.21	0.03	0.05	0.0089	0.036	trace	
Pb	0.98		0.02	0.025	< 0.025	trace	0.1-0.2
Co		0.095	0.01	0.0193	0.054		0.1
Ni		0.05	0.07	0.0210	0.092		0.1
SiO_2	4.28	1.06	3.81	2.62	2.93	12.68	15-20
Al_2O_3	0.86	4.67	5.42	3.00	4.52	2.15	
CaO + MgO	0.78	0.05	0.1	0.105	0.08	8.25	
BaO	2.37	0.37	0.15	2.34	0.28	trace	
$K_2O + Na_2O$	0.42	0.61	1.66	0.89	1.89	0.175	
CO_2		0.41		0.33	0.67	33.68	

[a] 1, Imini Mine, Morocco;
2, Moanda Mine, Gabon;
3, Kisenge, Zaire, Congo;
4, Groote Eylandt, Australia
5, Amapa Brazil
6, Ghana (N-grade carbonate)
7, Japan (High-grade carbonate)

TABLE XXVII

PRODUCTION AND PRICES OF SELECTED MANGANESE PRODUCTS

Product Name	Formula	Production capacity, t/yr World	Production capacity, t/yr U.S.	U.S. Price[a],$	Grade	U.S. Manufacture
Groote Eylandt Ore	MnO_2	70,000		74/t 77/t	Premium Fines	
Moanda Ore	MnO_2	100,000 for chemical uses		78/t 81/t	Metallurgy	
Moanda Ore	MnO_2	65,000		215/t	Battery	
Moroccan Ore	MnO_2	120,000		130/t	84 % grade	
Electrolytic (EMD) Manganese Dioxide	MnO_2	113,000	18,000	1,042/t	Battery	Kerr McGee(Union Carbide, ESB Covington
Chemical (CMD) Manganese Dioxide	MnO_2	27,000		1.58/kg	Faradiser M Battery	Sedema-Chemetals
High Purity Manganese Dioxide	MnO_2			1.32/kg	HP	Chemetals
High Purity Manganese (II) Oxide	MnO		9,000	1.76/kg	HP	Chemetals
Manganese (II) Oxide 60%	MnO	50,000	36,000	247/t	Feed Fertilizer	Chemetals, Eagle Picher, Union Caribde, Prince Mfg., American Minerals
Manganese Sulfate Manganese Sulfate	$MnSO_4$) $MnSO_4$)	128,000	41,000 27,000	165/t 281/t	Technical-fertilizer Feed-fertilizer (granular)	Tennessee Eastman Eagle Picher
Manganese Chloride	$MnCl_2$		3,000(est.)	1.47/kg	Anhydrous Flakes	Chemetals
Manganese Carbonate	$MnCO_3$	9,000		2.35/kg	45% Mn	Chemetals
Maneb	$MnC_4H_2N_2S_4$	136,000		2.42/kg	80% technical	DuPont, Rohm and Haas, Crystal Chemical Co.
Manganese Acetate Tetrahydrate	$MnOOCCH_3.4H_2O$	4,500		1.50/kg	Technical	Harshaw, Hall Chemical Co.

TABLE XXVII(Contd.)

PRODUCTION AND PRICES OF SELECTED MANGANESE PRODUCTS

Product Name	Formula	Production Capacity[a], t/yr World	U.S.	U.S. Price[b], $	Grade	U.S. Manufacture
MMT/CI-2	$C_9H_7Mn(CO)_3$		500-1,000(est.)	6.71/kg		Ethyl Corporation
Potassium Permanganate	$KMnO_4$	>40,000	14,000	1.87/kg	Technical	Carus Chemical Company
Potassium Permanganate	$KMnO_4$			2.31/kg	USP	Carus Chemical Company
Sodium Permanganate	$NaMnO_4.H_2O$		0.5	14.00 - 22.00/kg	Technical	Carus Chemical Company

[a] Largely based on actual quotes by suppliers in October, 1979.

7.6 Summary

Total world land based manganese reserves are estimated as 3,100 MM metric tonnes; the total sea bed reserves are 16,000 MM metric tonnes of contained manganese. All major North American land deposits are low grade. Seabed nodules off the Pacific Coasts of North and South America are rich in grade. Extraction is mainly performed on the latter by hydrometallurgical techniques and many companies are associated world wide with these processes, none, however, in Canada.

Directories are given of world-wide production of ferromanganese, silico-manganese and manganese metal as well as manganese dioxide and manganese chemicals.

The U.S. inventory of March 1981 upon which Canada places a large reliance is also shown in this section.

8. ALTERNATE SUPPLY OF MANGANESE FROM LOW-GRADE DEPOSITS AND WASTE STREAMS

8.1 Low-Grade Deposits

A listing of Canadian low-grade deposits was compiled by Energy, Mines and Resources Canada [27]. A summary of selected deposits by location, reserves and grade is given in Table XXVIII and includes information compiled by G.E. Viens [28].

Composition and origins of waste slags are shown in Table X, Section 4., P.20

8.2 Extraction of Manganese Values

Low-grade manganese ores do not respond to low-cost physical beneficiation methods such as gravity and magnetic separation or flotation treatments[29]. Thus, more expensive chemical dissolution methods are required to selectively extract the manganese values.

Use of diluted mineral acids requires a number of energy intensive steps including calcination to decompose carbonates or reductive roasts to convert MnO_2 to MnO, evaporation and crystallization to obtain manganese salts, as well as, thermal decomposition to produce Mn_3O_4. In addition acid regeneration units are required and corrosion and pollution controls add to the processing cost as well.

Leaching with SO_2[30] and NO_2[31] are less energy intensive as reduction roasts are eliminated and no acid regeneration is required. However, evaporation/crystallization and thermal decomposition, as well as corrosion and pollution problems need to be dealt with.

TABLE XXVIII

SELECTED CANADIAN LOW-GRADE MANGANESE ORE DEPOSITS

LOCATION	Reserves (Tons)	%Mn	% Fe	SiO_2	Al_2O_3	CaO	MgO	S	P	REMARKS
NEW BRUNSWICK Woodstock	200 Million	14-16	20-22	20	3.5	3.8	1.5	·/.	1.0	Carbonate Silicate Ore
NEWFOUNDLAND Manuels River	10 Million	5-10	1-5	-	-	-	-	-	-	Carbonate
NEWFOUNDLAND Brigus Bay		22.1	4.9	23.2	13.8	1.2	1.8	0.18	0.06	-
ONTARIO Steep Rock		13.6	53.6	3.2	1.2	·/.	·/.	·/.	0.2	-
QUEBEC Knob Lake		8-12	54-59	1.6-3.2	1.2-5.1	·/.	·/.	·/.	0.01	-
NOVA SCOTIA O'Handly	200,000	10-40	10-25	-	-	-	-	-	-	Manganese Dioxide Bog

While nitrogenous oxides present a real health hazard, the SO_2 system suffers from side reactions forming polythionates in addition to $MnSO_4$. This creates problems in the rotary kiln thermal dissociation to produce Mn_3O_4 at 1300°C. Additional problems have been experienced with gypsum scale forming in the leach vessel and control equipment.

The ammonia based leach systems [32] require reduced calcine to be effective and filtering of slimy hydrous oxide precipitates at controlled water additions is a problem. Excessive water usage requires expensive evaporation. The Dean process [33] permits rapid dissolution of manganese at concentrations of up to 100 gpL/manganese employing ammonium carbamate A crystalline, easily filterable carbonate precipitate can be obtained by addition of CO_2. This avoids expensive exporation/crystallization.

To make manganese silicate ores amenable to chemical dissolution an additional processing step is required, namely, melt-quenching or lime clinkering[34]. This all adds to the processing cost of making Mn_3O_4 from low-grade ores.

The basis of pyrometallurgical operations is selective smelting to produce pig iron containing the bulk of the phosphorous and a manganese oxide rich slag. In a second smelting operation, this slag is converted to standard ferromanganese or silicomanganese employing conventional submerged-arc or plasma furnace techniques. The problem, of course, is double processing with additional processing costs due to handling and melting a large quantity of inert gangue materials at temperatures of up to 1500°C or higher.

More recent developments concern the roasting of the manganese bearing shales with pyrite waste at 550°C to produce water soluble $MnSO_4$. This process was devised by Mandate Refinery Co. Canada Ltd. and takes into account the recovery of copper, zinc, lead, silver and gold. These elements were

originally present in the pyrite and are recoverable by hydrometallurgical methods. The main product is recovered as electrolytic manganese or Mn_3O_4 - smelter feed. Removal of copper and zinc from manganese bearing solutions by solvent extraction[35] enhances the Mandate approach.

Smelting of ore-carbon briquets in a cupola is being developed by MetKem Processes Ltd.[36]. This method has inherant economic advantages by using low-cost carbonaceous fines as fuel and reductant. The fact that the ambient gas composition in the furnace has little or no effect on the ore reduction rates and on degree of metallization[37] makes this approach even more attractive. This technique, once demonstrated on a specific manganese bearing feed material, can be retrofitted to existing cupolas with short lead times. Potential feed materials include manganese bearing discard slags (manganese present as silicate) and low or high-grade ores.

The technology for chemical beneficiation of low-grade manganese ores is summarized in Figure 5. Leaching is done with mineral acids, SO_2, NO_2 or ammonia based solutions.

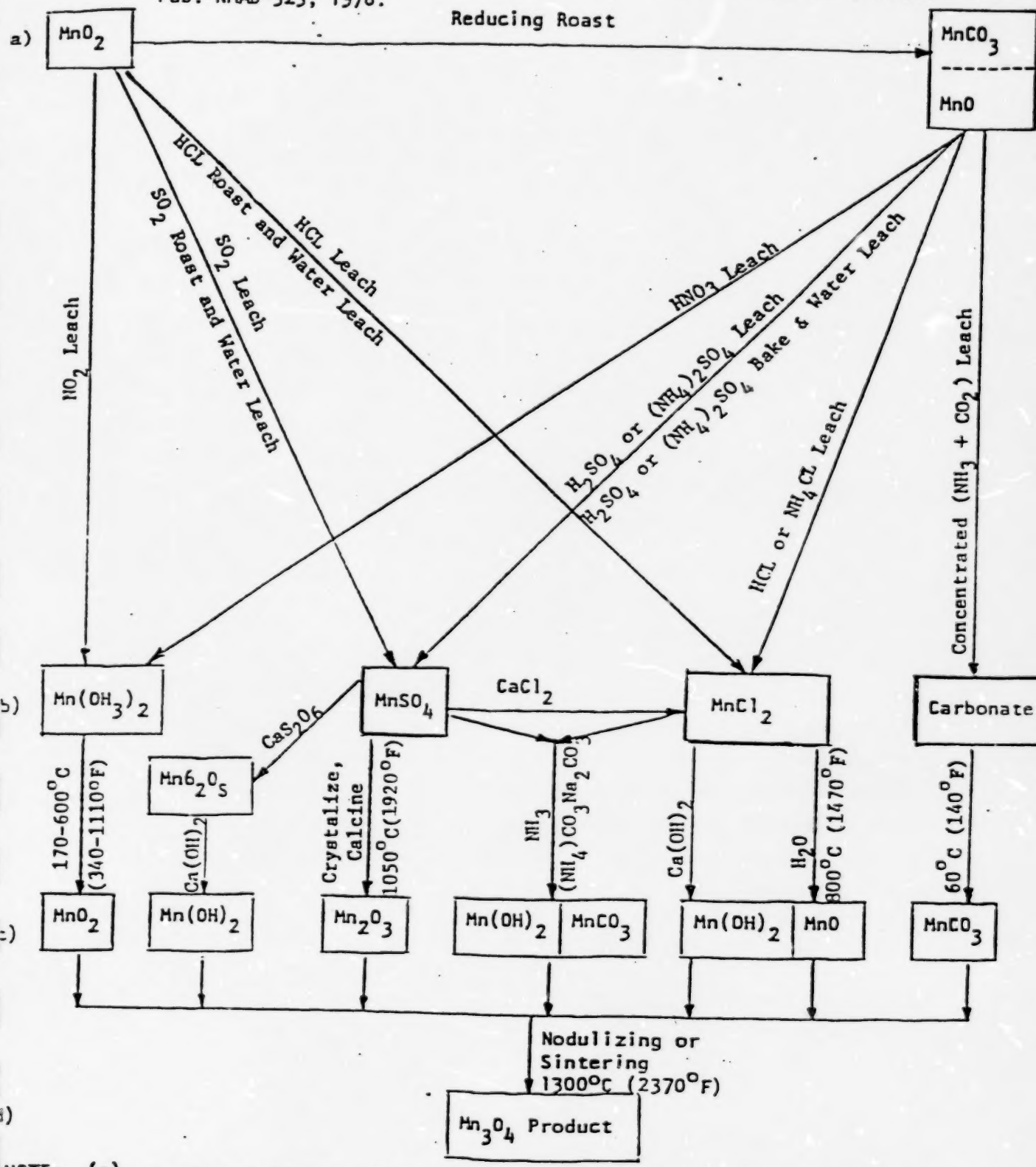
Following liquid/solid separation and purification of the various pregnant solutions, the resulting products recovered from solution (oxides, hydroxides, carbonates) are all converted at 1300°C to produce Mn_3O_4. This rather pure oxide in turn is being considered as feed for conventional submerged-arc smelting to produce standard ferromanganese, the main manganese product of commerce.

Since the extra costs incurred for chemical beneficiation dilute the profit margin of the smelter, none of these procedures have found commercial applications.

FIGURE 5

HYDROMETALLURGY OF MANGANESE

Taken from "Manganese Recovery Technology", National Advisory Board Pub. NMAB-323, 1976.



NOTE: (a) Mn mineral (intermediate oxides may be considered to behave essentially like mixtures of MnO_2 and MnO), (b) Solution, (c) Product recovered from solution, (d) Synthetic ferro-grade manganese ore.

A novel hydrometallurgical/pyrometallurgical process approach was developed by Ontario Research Foundation [38, 39, 40] that produces manganese carbide (Mn_7C_3) directly from manganese hydroxide precipitates. The resulting metallic carbide product can be used as an addition agent to steel. It is felt that this approach, once, scaled-up and optimized has sound economic features. Cost savings would be realized by making a finished product (Mn_7C_3) rather than feed material for smelting (Mn_3O_4). If found viable on a larger scale, this could eliminate the conventional smelting step.

The direct conversion of manganese precipitates to metallic carbide can be carried out in a rotary kiln or shaft furnace employing low cost carbonaceous materials for reduction and process heat generation.

8.3 Selection of Promising Procedures

Standard ferromanganese is presently being sold for 55¢/kg contained manganese. To meet the constraints for low processing costs the following requirements need to be met.

- Minimum number of unit operations
- Minimum number of high temperature operations
- Energy cost savings by using reactors of high thermal efficiency and/or use of low-grade coals as fuel and reductant
- Modern solution treatment methods need to be assessed to concentrate and recover manganese values
- Low-cost precipitation methods are preferred over evaporation/crystallization. In this connection, freeze crystallization should be considered as considerably less energy is required to freeze water than converting it to steam.

To meet the constraints of environmental and health concerns, processes that have the greatest promise of being technically and economically viable are the following:

(A) The Ammonium Carbamate (Dean) Process

This process permits rapid dissolution of MnO-based feed stocks at high Mn-concentrates in the leach liquor. Crystalline and easy filterable precipitates result. Energy intensive evaporation and crystallization operations are eliminated. Published processing costs based on pilot plant operations are quite encouraging. A combination of the carbamate dissolution and precipitation techniques with direct conversion of the wet precipitate with carbon to produce a metallic manganese carbide product are expected to yield even more favourable economics.

(B) The SO_2 Roast-Leach Process

No reductive roast is required for oxide and carbonate based ores. At 550-600°C, the predominant mineral species in the Woodstock ore (braunite, $3\ Mn_2O_3 \cdot MnO\ SiO_2$) decomposes and converts to water soluble $MnSO_4$ employing pyrite waste and air and/or SO_2 as sulphatizing agent. Formation of objectionable polythionates, from the environmental and process view points is eliminated. Direct conversion of manganese sulphate monohydrate to produce metallic manganese carbide and co-generation of SO_2 for recycle has not been tested as yet. In case of technical success, favourable economics should result.

(C) Cupola Smelting

While it has been demonstrated that iron can be smelted in a shaft furnace operated in the cupola mode of combustion using low cost carbon as fuel

and reducing agent, advantages for smelting low-grade manganese ores in a single pass are seen as follows:

- high hearth temperatures can be readily obtained
- expensive foundry coke ($180 - 200/ton coke) can be replaced with low-grade carbonaceous fuels ($15-40/ton)
- Based on exploratory reduction tests,[42] the prospects for producing throw-away slags containing 1-2% Mn are good.
- Manganese silicates can be readily processed.
- Short time frame can be realized by retrofitting smelting process to existing but modified cupolas.

(D) Plasma Processing

Plasma techniques have a potential for economic processing of low-grade ores.

The reasons are:

- Generation of very high temperatures at high energy efficiencies which in turn yields high productivity requiring smaller process units.
- Excellent control of atmosphere for efficient reduction
- Simple process control for lower operating costs.

Plasma devices employing entrained solids have not yielded encouraging results because of short retention times but torches that provide process heat for metal-slag type reactors have found commercial applications.

Westinghouse Applied Plasma Systems have developed megawatt units[46,47] that are being used by SKF in Sweden to produce direct reduced iron (Plasmared) and also to smelt iron ores (Plasmasmelt) for making hot metal.

The University of Toronto developed the Extended Arc Flash Reactor (EAFR) [48] and produced standard ferromanganese from slag successfully at a scale of 35 KW.

Electric power is a significant cost factor and projections have been made that power costs in the year 2000 will be twice that of fossil energy.

8.4 Summary

A listing of low-grade manganese deposits in Canada is given and some of the problems of extraction of manganese from domestic sources is enumerated. The promising processes are listed and some of the economical and technical reasons are given.

9. SUBSTITUTION OF MANGANESE

Manganese has become an essential element in steelmaking because of its ability to remove sulphur and oxygen and also to improve and control physical properties such as strength, toughness, hardenability and resistance to abrasion at a reasonable price.

9.1 Deoxidizing Agents

There are a number of metals having greater deoxidizing powers than manganese. In order of decreasing effectiveness these metals are:

- calcium
- magnesium
- aluminum
- titanium
- silicon
- manganese
- chromium

Apart from cost, the size, shape and melting points of the deoxidation products need to be considered as well as slag composition and treatment temperature before a selection of suitable deoxidizers can be made.

9.2 Desulphurizing Agents

Metals that form stable sulphides with stability factors greater than iron sulphide in order of decreasing affinity to sulphur are:

- calcium
- strontium
- barium
- oxygen
- manganese

- zinc
- cadmium
- molybdenum
- iron

Again, consideration must be given to the physical properties of the formed sulphide. Machining properties of steel treated with substitute desulpharizers is another concern.

9.3 Hardenability

The hardenability factors for a number of alloying elements relative to values for pure iron-carbon alloys are known and published [43].

According to Figure 6 manganese has the highest factor followed by molybdenum, chromium, silicon and nickel, at any given addition levels.

Based on these relationships empirical formulas for carbon equivalent were developed

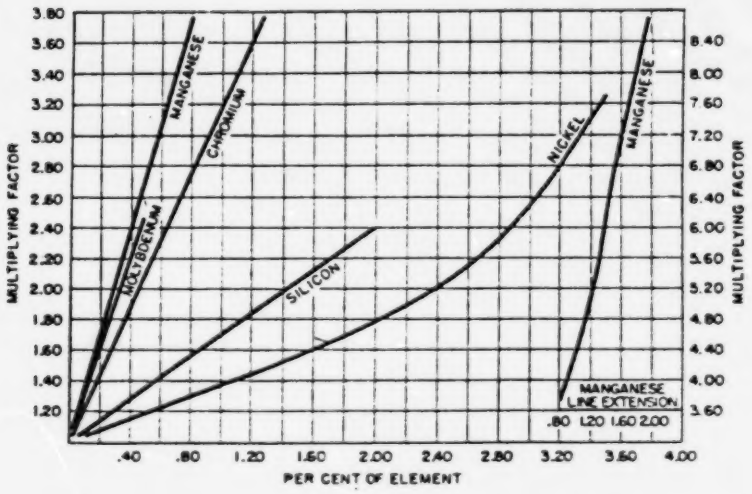
$$C.E. = \%C + \frac{\%Mn}{6} + \frac{\%Cr + \%V}{5} + \frac{\%Ni + \%Cu}{15} + \frac{\%Mo}{4}$$

These data can be used as a guide to compute substitute alloying elements for manganese. It should be noted that hardenability depends on other factors as well, including phosphorous content and grain size of steel.

9.4 Other Considerations

Substitute alloying elements will profoundly change the iron-carbon phase diagram. Nickel, cobalt, copper, carbon and nitrogen will enhance the retention of the austenite phase same as manganese. Elements such as chromium, silicon, molybdenum, tungsten, vanadium, tin, columbium, phosphorus, aluminum and titanium on the other hand enhance ferrite formation.

FIGURE 6



Multiplying factors for a variety of alloying elements (American Iron and Steel Institute).

Corrosion, abrasion and magnetic properties may also be affected by these alloying elements.

It becomes apparent that there are many options for substitution for a given type of steel or among different types of steels. For this reason it was recommended by the U.S. National Materials Advisory Board[44] to "stockpile" available information on substitution applications. International Harvester Company, for instance relies on Computer designed steels such as Mn-Cr grades SAE EX58 to EX62.

9.5 Summary

Manganese is an essential element in steelmaking. As a deoxidizer manganese is not as effective as some of the other elements, however, its melting point, slag forming properties etc. must be taken into account and because of this manganese is considered an excellent deoxidizer. As a desulphurizer manganese is excellent since the form and physical properties of the sulphide are of primary importance. Free machining steels containing manganese sulphide are the least expensive. Manganese is the best alloying agent used for hardening steel. It is followed by molybdenum, chromium, silicon and nickel. Chromium is being substituted for manganese in some abrasion resistant steels since some of its properties are better than Hadfield Steel. There are many alloying options in steels that can be used and information is being collected in the U.S. on substitution alloying materials to reduce the impact of short supply of critical elements.

10. SUMMARY AND CONCLUSIONS

10.1 Principal Manganese Products

These fall into the main groups of sub-products:

(1) Metallic manganese in both elemental form and as ferromanganese and silicomanganese

(2) Manganese dioxide as both electrolytic manganese dioxide (EMD) and chemical manganese dioxide (CMD) and

(3) Various manganese chemicals

10.2 Consumption of Manganese

Canadian consumption of manganese ore, all of which is imported, 1978 and 1979 amounted to over 200,000 tonnes in 1978 and over 60,000 tonnes in 1979. Almost all was used in the metallurgical industry. World consumption of manganese ore was 9 MM tonnes in 1977 and it is estimated that this will increase at a rate of 2.9%/year to 21 MM tonnes in the year 2000.

In steel, manganese acts as desulphurizer and deoxidizer and as an alloying addition to improve physical properties such as hardenability, toughness and abrasion resistance.

Manganese is also used as an alloying agent in aluminum. Non-metallic uses of manganese are mainly dry-cell batteries and as a colourant for ceramics.

10.3 Canadian Manufacture of Manganese Products

The consumption of domestically produced ferromanganese and silicomanganese is dropping but the importation of both materials is increasing. Union Carbide, Canada's largest producer of ferromanganese, imports most of its ore from Brazil, South Africa and Gabon. Union Carbide also stockpiles over 100,000 tons of manganese slag in Quebec from its own operation.

Its production is about 50,000 tons of HC Ferromanganese and 16,000 tons of silicomanganese per year. There is no manufacturer of EMD or CMD or manganese chemical products in Canada.

10.4 Possible Domestic Sources

Canada has about 15.9×10^6 metric tons of manganese contained in low grade ores as reserves which is about 0.5% of the world reserves. The manganese ores average between 3 and 16% Mn and are found in Eastern Canada, New Brunswick, New Foundland, Nova Scotia, Ontario and Quebec.

High energy and costly processes are necessary for producing standard manganese products from these ores unless a manganese carbide is produced instead of ferromanganese.

10.5 Substitutes

Other elements can be used instead of manganese for deoxidizing and desulphurizing steel. However, in most cases these elements are not so handy or inexpensive as manganese and, where manganese is being used as a hardening or toughening agent, the substitution of chromium is unfortunate since it is also considered a strategic material.

The substitution of manganese in aluminum would not seem to be much of a problem due to its comparatively low volume and low percentage addition to aluminum alloys.

No consideration has been given to the substitution of manganese oxide in dry-cell batteries since the substitution of other compounds changes the nature of the cell.

10.6 Stocks

The producers of ferromanganese and silicomanganese stockpile minor quantities of imported ore from year to year and also stockpile manganese bearing slags, containing between 25 - 45% manganese. This is about nine months supply for the ferromanganese and silicomanganese makers.

U.S. stockpiles are comparatively healthy and most Canadian producers are relying on this, certainly in the short term. The U.S. inventory exceeds its set goals except in the case of manganese ore where it is marginally down. (March 1981 figures).

10.7 Possible Courses of Action

If the supply of manganese ore and products from off-shore sources is curtailed, Table XXIX gives the possible courses of action.

11. RECOMMENDATIONS

It is recommended that quick consideration is given to the methods for the extraction of manganese from low-grade domestic deposits. This should cover the feasibility of using an easier and cheaper method to produce manganese carbide rather than just upgrading the ore to a purer manganese oxide.

It is also recommended that a careful assessment be made of the substitution elements in steel and their advantages and disadvantages.

W. G. Brandstatter, P. Eng.
Assistant Director
Department of Engineering
and Metallurgy

HGB:aac
May 14, 1982

TABLE XXIX

	Expected Duration of Interruption	Manganese Ore	Ferromanganese and Silicomanganese	Battery Grade MnO_2
A.	Up to six months	Obtain from U.S.A.	Obtain from U.S.A. or increase Canadian output using U.S. ore	Obtain from U.S.A
B.	Six months to two years	As above or Try to develop new sources	As above or use new ore sources. Smelt slag for silicomanganese.	As above
C.	Two to five years	As above Develop use of low grade Canadian Manganese ores	As above U.S. may have developed sea bed nodules (extraction) and may export ferromanganese . Use manganese carbide as substitute material	As above Develop methods for extraction of manganese dioxide from Canadian low-grade ores.
D.	Over five years	Build large facilities for using Canadian low grade ores	As above	Develop a Canadian industry for manufacturing CMD or EMD

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